

THE EISENHOWER LIBRARY



3 1151 02690 2530

163.354

Library



Johns Hopkins University  
of the





















A STUDY OF THE CONDUCTIVITY AND DISSOCIATION OF  
CERTAIN ORGANIC ACIDS IN AQUEOUS SOLUTION  
AT DIFFERENT TEMPERATURES.

-:-

DISSERTATION

Submitted to the Board of University Studies  
of The Johns Hopkins University in Conformity  
with the Requirements for the Degree of Doc-  
tor of Philosophy.

---

By

Alfred Springer, Jr.

Baltimore, June, 1912.

-:-

163354

T 5 11. VII 1942

## CONTENTS.

-:-

	Page
Acknowledgment.	
Introduction.....	1
Procedure.....	3
Limiting Conductivity of Acids.....	11
Tables of Conductivity, Data for Acids.....	14
Discussion of Results.....	42
Summary.....	54
Biography.	





# ACKNOWLEDGMENT.

-:-

To Professor Jones, at whose suggestion and under whose guidance this investigation was carried on, sincere thanks are offered by the author. No less gratitude is due President Remsen, Professors Morse, Jones, Acree and Whitehead, and Associate Professor Lovelace for instruction in the lecture room and in the laboratory.



A STUDY OF THE CONDUCTIVITY AND DISSOCIATION OF  
CERTAIN ORGANIC ACIDS IN AQUEOUS SOLUTION  
AT DIFFERENT TEMPERATURES.

--:-

Introduction.

A careful review of the work, previously done on the conductivity and dissociation of organic acids in aqueous solution, has already been made by White and Jones (1) and by Wightman and Jones.(2) So any historical sketch, which we might give at this point, would be superfluous. We shall therefore proceed at once to the experimental part of our work, and, in the discussion which follows, reference will be made to all important articles having direct bearing on our results.

This particular investigation has been in progress for somewhat more than two years. During the first year conductivity measurements were made at temperatures between zero and thirty-five degrees. During the second year the conductivities of the same acids--as well as some already used by White and Jones at lower temperatures--were taken at temperatures ranging from thirty-five to sixty-five degrees. The two sets of results at thirty-five degrees were compared, and in this method we had a check on the work of two different years. Some of these agreements and disagreements will be tabulated in another place. The two sets of measurements, for any given acid, were made with different apparatus, different

---

(1) Am. Chem. J. 44, 159 (1910).

(2) Ibid 46. 56 (1911).



solutions, usually with different specimens of the acid, and frequently by different investigators.

### Reagents.

The water used in all this work was prepared in the manner always employed in this laboratory, and adequately described by Jones and Mackay. (1)

The acids used were obtained in most cases from Kahlbaum. They were, with one exception, purified by filtration and recrystallization from the conductivity water. Before weighing they were always carefully dried over sulphuric acid in a vacuum dessicator. Their melting points were taken, whenever possible, as a test of their purity. The most concentrated solution used was made up by direct weighing, and standardized by titration against a solution of sodium hydroxide. The only acid, which we could not treat in this manner was dichlor acetic. This we did not purify at all, as it was the best obtainable--having been distilled from chloral. Being a liquid at ordinary temperatures, and hygroscopic, it could not be weighed accurately. So the mother solution was prepared by the usual titration method.

### Apparatus.

The conductivity cells were of the type used by Jones and Bingham. (2) Briefly, these have platinum electrodes

---

(1) Am. Chem. J. 19, 91. Z. physik. Chem. 22, 237.

(2) Am. Chem. J. 34, 493 (1905).





(always coated with platinum black) attached to glass tubes containing mercury; the tubes being sealed into ground glass stoppers. A special cylindrical type of cell (1) was used for determining the conductivity of the water.

The cell constants were taken in the manner described by White and Jones. During the low temperature work the cells were standardized about once a month. While working at elevated temperatures this was done even more frequently.

When this investigation was begun, an ordinary Wheatstone bridge was employed. Soon, however, we secured from Leeds and Northrup a very fine Kohlrausch slide-wire bridge, by means of which it was possible to read to fractions of a millimeter.

The resistance box, thermometers, thermostats, and other apparatus scarcely merit description. In general, all the precautions were taken, which Wightman and Jones recommend.

#### Procedure.

The method of procedure for measurements at the lower temperatures has already been described in many papers from this laboratory.

But at the more elevated temperatures much less has been done. Clover and Jones (2) and West and Jones (3) are our only predecessors. A brief review of their work might not be out of place here.

---

(1) Ibid . 45, 282 (1911).

(2) Am. Chem. J. 43, 187 (1910).

(3) Ibid. 44, 508 (1911).



Clover and Jones encountered a number of difficulties, in their higher temperature measurements, which had never been noticed in the lower temperature work. The cell constants changed frequently. The solubility of the glass was noticeable. The coefficient of expansion of water had to be taken into consideration. How they coped with these problems will be seen from the following quotations, taken from their paper-- Cell constants. "It has developed that a strain is brought about by the high temperatures, which may result in a change either in the distance of the electrode plates from each other, or in the surface of the plates.

"Since such a variation had not previously been observed in work covering a range from  $0^{\circ}$  to  $35^{\circ}$ , it was thought that the changes might be reduced by maintaining the cells at a temperature which was about a mean of those employed in the experimental work. Accordingly, when not in use, the cells were filled with pure water and placed in a bath which was maintained continuously at a temperature of  $45^{\circ}$  to  $50^{\circ}$ ."

They then describe the following experiment:

"The measurements were first carefully made at  $35^{\circ}$  and duplicated; then the regular systematic procedure was gone through at  $65^{\circ}$ , and after this the readings at  $35^{\circ}$  were again made. If the results obtained the second time should agree with those first obtained at  $35^{\circ}$ , this would be strong evidence that the method was reliable. It was found in some cases that the second reading differed slightly from the first. In other cases there was no difference, and the change appeared to be independent of the cell used, or the



concentration of the solution. It was found, further, that on standing for a considerable length of time at  $35^{\circ}$  (2 or 3 hours) the reading slowly changed back in all cases to the original value. It is difficult to see what other cause can be assigned to these results than a temporary change in the cell constant during the heating at  $65^{\circ}$ ."

Solubility of Glass. "In conductivity work at ordinary temperatures this factor has always been neglected, and probably is not sufficiently large to influence the results even with very dilute solutions. However, at  $50^{\circ}$  the error introduced by this factor at a dilution of 1000 is greater than any of the other ordinary experimental errors. At  $65^{\circ}$  the solubility of the glass is still greater, and at  $80^{\circ}$  the conductivity of pure water is increased tenfold on remaining in the cell for a couple of hours. In this connection it may be stated that the cells employed were made of hard glass. Of course, the amount of glass dissolved depends upon the exact nature of the latter, and was found to vary considerably with the different cells used, and at different intervals in the case of any one cell. The idea of introducing a correction for the solubility of the glass was abandoned, but the difficulty was overcome in another way. It was found that after the cells had been heated with water for several days the amount of glass dissolved gradually decreased and finally amounted to practically nothing. After this treatment, as the cells were kept in a bath at  $45^{\circ}$  to  $50^{\circ}$  and the water in them changed once a day, the solubility of the glass





at 65° was always practically nothing, or entirely negligible. If a cell were removed from the bath and allowed to stand filled with water at room temperature for any length of time, it was found that glass was again dissolved on heating."

Because of the great increase of the coefficient of expansion of water with rising temperature, Clover and Jones found it necessary to make up the solutions at the exact temperature at which they were to be measured. That is--for the same acid, one set of solutions was prepared at 50° and another at 65°. The solutions prepared at the former temperature were also used for measurements at 35°, and the correction factor 0.994 was then applied.

It was found advisable to nearly fill the cells with the solution for the following reasons: "First, to minimize any slight change in concentration brought about by condensation or escape of the solvent, or from any other cause. Second, to exclude the air with its accompanying carbon dioxide from the cell, as the dioxide would be dissolved during the manipulation and would influence the results with dilute solutions. Third, to prevent difficulty in opening the cells. with a large air space diminished pressure is quickly produced on removal from the bath, and if the cells can be opened at all it can be done only at the risk of distorting the electrodes."

In the following year west and Jones took up again the problem of conductivity measurements at relatively high temperatures. They found that by heating the glass vessels first with dilute sodium hydroxide, then with dilute hydrochloric acid, and lastly with conductivity water, the solubility of



the glass could be reduced to a negligible quantity.

They also devised the following method for determining the cell constants: "The standard solution of potassium chloride was placed in the cell. The cell was then heated to  $50^{\circ}$ , and after remaining at that temperature for about an hour was cooled to  $20^{\circ}$ . As soon as temperature equilibrium was established at  $20^{\circ}$  the conductivity readings were made and the cell constants calculated." In this manner the constants of the cells, with electrodes and everything in the  $50^{\circ}$  position, were taken at  $20^{\circ}$ , where the conductivity of the standard potassium chloride is known. Clover and Jones had previously found (as stated above) that the cells would be required to stand in a  $20^{\circ}$  bath for several hours before their electrodes would resume the  $20^{\circ}$  position.

Probably the most beneficial contribution, that West and Jones gave to this work, was their method for preparing solutions. This brief quotation explains both the method and its advantages.

"Since we worked over a range of temperature of only  $30^{\circ}$ , we found it convenient to prepare the solutions at the intermediate temperature,  $50^{\circ}$ , and then to use the solutions at the three temperatures,  $35^{\circ}$ ,  $50^{\circ}$  and  $65^{\circ}$ . But since the volume of a solution varies with the temperature it was, of course, necessary to apply a correction at  $35^{\circ}$  and  $65^{\circ}$  to the volume of solutions made up at  $50^{\circ}$ .

"When a standard solution is cooled from  $50^{\circ}$  to  $35^{\circ}$  there is a contraction in volume and a consequent increase in the



concentration of the solution. The value of  $M_v$  for any solution would, therefore, be slightly too large. The value of  $M_v$  as found must be multiplied by the factor 0.994 for results at  $35^\circ$  when the solutions were made up at  $50^\circ$ . The correction factor for solutions made up at  $50^\circ$  and used at  $65^\circ$  is 1.0076.

"The coefficient of expansion for distilled water is somewhat less than that for an aqueous solution. However, the difference in the coefficients for water and for our most concentrated solution is so small that it is negligible.

"By making use of the above correction it was necessary to prepare only one set of solutions for each salt; and, consequently, much pure material and time were saved."

When we began the investigation at higher temperatures these two questions presented themselves:

First:- If the cells give evidence of soluble glass whenever they are heated to  $50^\circ$ , cooled to room temperature, and then heated to  $50^\circ$  again, will not the measuring flasks show this same tendency? For the measuring flasks are not kept in the heated bath, when not in use.

And Second:- When a solution at  $50^\circ$  is poured into a burette, then transferred to a measuring flask slowly, so that the burette may drain, what will be its temperature at the end of the procedure? Clearly not  $50^\circ$ , since a burette has a large surface in contact with the cool air of the room. And the process of draining at best must require two minutes or more. So when the experimenter imagines he is drawing off





X cubic centimeters at  $50^{\circ}$ , he is actually drawing off X cubic centimeters at some lower temperature--which is the same as more than X cubic centimeters at  $50^{\circ}$ .

A simple device did away with both these possible sources of error. At  $50^{\circ}$ , 988.07 grams of distilled water have a volume of 1000 cubic centimeters. Our liter flask was weighed at  $20^{\circ}$ . 988.07 grams of distilled water at  $20^{\circ}$  were introduced--air displacement being taken into account. The flask was marked at the bottom of the meniscus. This flask filled to the mark with water at  $20^{\circ}$  (room temperature) will contain a liter at  $50^{\circ}$ . Therefore all the mother solutions could be made up for  $50^{\circ}$  work at  $20^{\circ}$ . And the solubility of the glass, which is noticeable only at higher temperatures is thus made negligible.

This mother solution will be, let us say, normal at  $50^{\circ}$ . At  $20^{\circ}$  it is stronger than normal. If we draw out 100 cubic centimeters at  $20^{\circ}$ , and dilute it to a volume of 200 cubic centimeters at  $20^{\circ}$  it will also be stronger than half normal. But heat this latter solution to  $50^{\circ}$  and it will again attain its required normality--assuming that the coefficient of expansion of water is the same as that of dilute solutions. And all solutions worked with were eighth normal or more dilute. This permits us to titrate all solutions at room temperature, which obviates the second of the above difficulties.

The values of the limiting conductivities ( $\kappa_{\infty}$ ) of the monobasic organic acids were calculated from the  $\mu_{\infty}$  of their sodium salts. This well known method consists merely in de-



ducting the migration velocity of the sodium ion from the value of the sodium salt, and in substituting in its place the migration velocity of the hydrogen ion. The equation of Schaller <sup>(1)</sup> is self-explanatory.

$$\mu_{\infty}(\text{acid}) = \mu_{\infty}(\text{Na salt of acid}) - \mu_{\infty}(\text{NaCl}) + \mu_{\infty}(\text{HCl})$$

The  $\mu_{\infty}$  values for hydrochloric acid and sodium chloride have been determined by previous workers. The sodium salt of the acid in question was made by titration of the acid with sodium hydroxide from alcohol--phenolphthalein being used as an indicator. Only solutions of a concentration of N/2048 were used, since it was found by White and Jones <sup>(2)</sup> that the  $\mu_{\infty}$  values of the sodium salts generally occur at this concentration.

For dibasic organic acids the  $\mu_{\infty}$  of the sodium salt can not be directly determined. Ostwald <sup>(3)</sup> has however described a satisfactory method for obtaining the value of  $\mu_{\infty}$  for the acid. Dibasic acids, he says, in most cases dissociate like monobasic acids--setting free only one hydrogen cation. And the limiting conductivities of monobasic acids seem to be a function of the number of atoms contained in the anions. So a dibasic acid having 16 atoms should give the same  $\mu_{\infty}$  value as a monobasic acid containing 16 atoms. And the latter value can be experimentally obtained.

The following table shows the limiting conductivities of all the acids with which we worked. These acids are arranged in the order of the number of atoms contained in their molecule. The values for the dibasic acids were worked out as described above.

---

(1) Z. physik. Chem. 25, 497 (1898).

(2) Am. Chem. J. 44, 161 (1910).

(3) Z. physik. Chem. 1, 74 (1887).



## LIMITING CONDUCTIVITIES.

-:-

Acid	Atoms	0°	15°	25°	35°	50°	65°
Dichloro- acetic	8	221.7	305.6	359.3	408.7	477.3	545.8
Bromo- succinic	10	222.2	302.1	354.1	-----	-----	-----
Pyromucic	12	223*	-----	355*	405	471	539.2
Salicylic	16	-----	-----	-----	403	472.5	539
Phenyl- propionic	17	222.2	300.4	352	400	470	539
Dimethyl- malonic	17	222.2	300.4	352	400	470	539
Ethyl- malonic	17	222.2	300.4	352	400	470	539
o-Phthalic	18	-----	-----	---	400	470	538.8
Sulphanilic	18	222*	-----	350.9	400	470	538.8
Metanilic	18	222*	-----	350.9	400	470	538.8
Phenyl- acetic	18	-----	-----	-----	400	466	535.2
Allyl- malonic	18	221.4	299.3	350.9	400	468	537
Cinnamic	19	-----	-----	-----	399.2	470	537.2
Dinitro- amino- phenol	19	221.7	299.1	350.2	399	470	537.2
Anisic	19	221.7	299.1	350.2	399	470	537.2
Vanillic	20	221.3	299.1	349.8	397.3	464	532.8
Coumaric	20	220.9	298.9	349.8	397.9	468.	534.4
Methyl- ethyl- malonic	20	221	299	349.8	397.3	464	533
Isopropyl- malonic	20	221	299	349.8	397.3	464	533
Hydro- cinnamic	21	220.8	298.9	349.7	397.2	463.5	532.6
Acetyl- salicylic	21	220.8	297.4	344.4	397.9	463.5	-----
Diethyl- malonic	23	219.4	296.1	346.2	393.9	464.8	533.9
Butyl- malonic	23	219.4	296.1	346.2	393.9	464.8	533.9
Benzyl- malonic	24	219	295.6	345.7	393.2	464	533
Naphthionic	24	221.9	296.3	352.2	401.1	468	534.5
Dipropyl- malonic	29	218.6	295.1	345.7	392.8	458	520

The four asterisked values--pyromucic acid at 0° and 25° and sulphanilic and metanilic acids at 0°--are taken from the



data of White and Jones. (1) At 35° their values coincide exactly with ours.

Dibrom succinic and sulphosalicylic acids are omitted from the above list. As may be seen from their conductivities they do not dissociate as monobasic acids, so the method of Ostwald for finding their  $\mathcal{M}_{\infty}$  could not be employed.

Measurements with bromsuccinic and acetyl salicylic acids could not be completed at higher temperatures, because these acids decomposed.

The sodium salt of dinitro aminophenol could not be made by titration, because of the depth of color of its solution.

No indicator was necessary in the case of (o) coumaric acid--the solution itself turning green when neutralized with sodium hydroxide.

It will be seen from the above table that the values for  $\mathcal{M}_{\infty}$  decrease pretty regularly. A curve, in which the ordinates represent  $\mathcal{M}_{\infty}$  values, and the abscissae the number of atoms, shows this relation very nicely. The following diagram was plotted in this manner--  $\mathcal{M}_{\infty}$  values for monobasic acids at 25° and 65° being used as examples.

### Results.

The results of our conductivity measurements are tabulated in the following pages. The molecular conductivities ( $\mathcal{M}_v$ ) are express in Siemen's units.

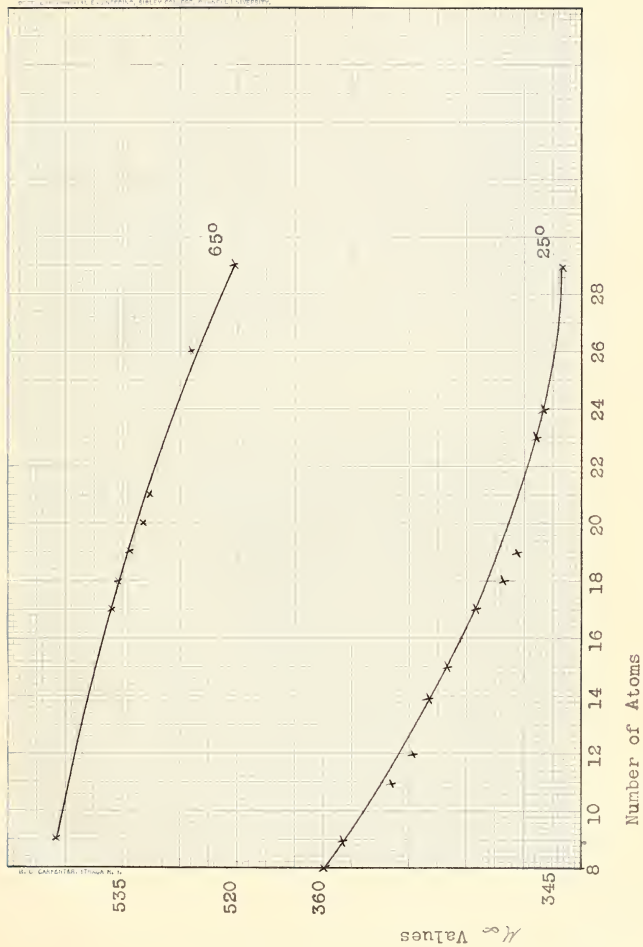
The Temperature Coefficients expressed in conductivity  
Units ;=  $\frac{\mathcal{M}_t - \mathcal{M}_t}{t_1 - t}$

---

(1) Am. Chem. J., 44, 163 (1910).







LIMITING CONDUCTIVITIES.



And the percentage temperature coefficients =  $\frac{\text{Cond. units}}{\mu_t}$ ,  
 where  $t$  is the one temperature,  
 $t_1$  the next higher temperature measured,  
 $\mu_t$  and  $\mu_{t_1}$  the conductivities for the same solution, measured  
 at temperatures  $t$  and  $t_1$  respectively.

Percentage dissociation ( $\alpha$ ) is of course  $\frac{\mu_v}{\mu_{\infty}}$

The dissociation constants ( $K$ ) =  $\frac{\alpha^2}{(1-\alpha)^v}$ , which is the  
 Ostwald dilution law.



DICHLORACETIC ACID.  $\text{CHCl}_2\text{.COOH.}$ 

-:-

Molecular Conductivity.

v	0°	15°	25°	35°	50°	65°
32	166.0	220.3	253.9	286.9	330.8	356.8
128	203.7	272.6	318.0	360.4	418.3	453.3
512	220.5	300.0	352.8	403.8	468.6	528.4
1024	221.7	305.6	359.3	408.7	470.0	535.8
2048	217.0	302.1	358.1	408.5	477.3	545.8

Temperature Coefficients (Cond. units)

v	0-15°	15-25°	25-35°	35-50°	50-65°
32	3.62	3.36	3.30	2.93	1.75
128	4.59	4.54	4.24	3.86	2.33
512	5.30	5.28	5.10	4.19	3.99
1024	5.46	5.37	4.94	4.09	4.39
2048	5.67	5.60	5.04	4.59	4.57

Temperature Coefficients (Per cent)

v	0-15°	15-25°	25-35°	35-50°	50-65°
32	2.18	1.53	1.30	1.02	.52
128	2.25	1.66	1.33	1.07	.56
512	2.41	1.76	1.43	1.04	.87
1024	2.46	1.75	1.37	1.00	.90
2048	2.61	1.85	1.41	1.12	.95

Percentage Dissociation.

v	0°	15°	25°	35°	50°	65°
32	74.87	72.09	70.67	70.20	69.32	65.37
128	91.88	89.20	88.51	88.12	87.64	83.05
512	99.46	98.17	98.18	98.80	98.18	96.81
1024	100.00	100.00	100.00	100.00	98.47	98.17
2048					100.00	100.00



PHENYLACETIC ACID.  $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{COOH}$ .

--

Molecular Conductivity.

v	35°	50°	65°
32	15.81	17.79	19.26
128	30.86	34.75	37.53
512	58.60	65.64	70.98
1024	78.80	88.31	95.18
2048	106.1	120.0	130.0

Temperature Coefficients (Cond. units)

v	35-50°	50-65°
32	.132	.098
128	.260	.185
512	.470	.356
1024	.634	.451
2048	.926	.666

Temperature Coefficients (Per cent)

v	35-50°	50-65°
32	.83	.55
128	.84	.49
512	.80	.54
1024	.80	.51
2048	.87	.55

Percentage Dissociation.

v	35°	50°	65°
32	3.95	3.86	3.60
128	7.72	7.46	7.01
512	14.65	14.08	13.26
1024	19.70	18.95	17.78
2048	26.53	25.75	24.29

Dissociation Constants.

v	35°	50°	65°
32	.507	.484	.420
128	.505	.470	.413
512	.491	.451	.396
1024	.472	.433	.375
2048	.468	.436	.381





ETHYLMALONIC ACID.  $\text{C}_2\text{H}_5\text{CH}(\text{COOH})_2$ .

## Molecular Conductivity.

$\nu$	$0^\circ$	$15^\circ$	$25^\circ$	$35^\circ$	$50^\circ$	$65^\circ$
8	20.85	28.08	32.62	36.64	41.67	46.09
32	40.90	55.22	64.42	72.53	82.52	90.66
128	73.08	98.35	114.55	129.09	146.60	161.77
512	119.8	161.7	188.9	213.0	243.3	269.9
1024	146.4	197.8	231.2	260.0	297.9	330.6
2048	166.7	225.4	263.5	298.3	345.3	384.7

Temperature Coefficients (Cond. units)

$\nu$	$0-15^\circ$	$15-25^\circ$	$25-35^\circ$	$35-50^\circ$	$50-65^\circ$
8	.48	.45	.40	.33	.29
32	.95	.92	.81	.67	.54
128	1.68	1.62	1.45	1.17	1.01
512	2.79	2.72	2.41	2.02	1.64
1024	3.42	3.34	2.88	2.53	2.18
2048	3.91	3.81	3.48	3.13	2.63

Temperature Coefficients (Per cent)

$\nu$	$0-15^\circ$	$15-25^\circ$	$25-35^\circ$	$35-50^\circ$	$50-65^\circ$
8	2.31	1.61	1.23	.91	.71
32	2.33	1.66	1.27	.92	.66
128	2.30	1.65	1.26	.90	.66
512	2.33	1.68	1.27	.95	.67
1024	2.33	1.69	1.25	.97	.71
2048	2.35	1.69	1.32	1.04	.76

Percentage Dissociation.

$\nu$	$0^\circ$	$15^\circ$	$25^\circ$	$35^\circ$	$50^\circ$	$65^\circ$
8	9.38	9.34	9.27	9.17	8.85	8.55
32	18.41	18.38	18.31	18.15	17.56	16.82
128	32.89	32.73	32.56	32.30	31.20	30.01
512	53.93	53.82	53.70	53.30	51.77	50.08
1024	65.91	65.83	65.72	65.06	63.40	61.34
2048	75.04	75.00	74.91	74.65	73.47	71.37

Dissociation Constants.

$\nu$	$0^\circ$	$15^\circ$	$25^\circ$	$35^\circ$	$50^\circ$	$65^\circ$
8	12.1	12.0	11.8	11.6	10.7	10.0
32	12.9	12.9	12.8	12.5	11.6	10.6
128	12.6	12.4	12.3	12.0	11.0	10.0
512	12.3	12.2	12.2	11.9	10.9	9.8
1024	12.4	12.3	12.3	11.8	10.7	9.5



ISOPROPYLMALONIC ACID.  $(\text{CH}_3)_2\text{CH}.\text{CH}(\text{COOH})_2$ .

## Molecular conductivity.

$\nu$	0°	15°	25°	35°	50°	65°
32	40.07	54.69	64.92	73.63	84.05	91.73
128	72.21	98.65	117.00	132.34	151.88	168.00
512	118.6	161.6	192.9	217.6	248.8	278.4
1024	144.1	197.0	234.0	264.4	307.7	343.8
2048	167.4	228.9	272.2	307.9	357.0	402.5

## Temperature Coefficients (Cond. units)

$\nu$	0-15°	15-25°	25-35°	35-50°	50-65°
32	.97	1.02	.87	.69	.51
128	1.76	1.83	1.53	1.30	1.07
512	2.86	3.14	2.47	2.08	1.97
1024	3.53	3.70	3.04	2.89	2.41
2048	4.10	4.32	3.77	3.27	3.03

## Temperature Coefficients (Per cent)

$\nu$	0-15°	15-25°	25-35°	35-50°	50-65°
32	2.43	1.87	1.34	.94	.61
128	2.43	1.86	1.31	.98	.71
512	2.41	1.88	1.28	.96	.79
1024	2.45	1.88	1.30	.92	.78
2048	2.45	1.88	1.38	1.06	.85

## Percentage Dissociation.

$\nu$	0°	15°	25°	35°	50°	65°
32	18.14	18.29	18.56	18.50	18.11	17.21
128	32.69	33.00	33.45	33.26	32.73	31.52
512	53.70	54.04	55.15	54.69	53.62	52.23
1024	65.24	65.89	66.89	66.44	66.31	64.50
2048	75.79	76.59	77.80	77.30	76.94	75.51

## Dissociation Constants.

$\nu$	0°	15°	25°	35°	50°	65°
32	12.5	12.8	13.2	13.1	12.5	11.2
128	12.4	12.7	13.1	12.9	12.5	11.3
512	12.2	12.4	13.2	12.9	12.1	11.2
1024	12.0	12.4	13.2	12.8	12.5	11.4
2048	11.6	12.2	13.3	12.9	12.5	11.3



n. BUTYLMALONIC ACID.  $C_4H_9CH.(COOH)_2$

—:—  
Molecular Conductivity.

v	0°	15°	25°	35°	50°	65°
32	37.53	50.60	58.72	66.30	76.00	83.93
128	68.80	92.04	107.34	121.86	141.00	156.00
512	113.8	154.20	180.9	204.8	236.2	264.2
1024	140.0	187.2	218.3	248.0	286.2	320.1
2048	163.7	218.8	255.4	291.3	340.0	382.6

Temperature Coefficients (Cond. units)

v	0-15°	15-25°	25-35°	35-50°	50-65°
32	.87	.81	.78	.65	.53
128	1.55	1.53	1.45	1.28	1.00
512	2.69	2.67	2.39	2.09	1.87
1024	3.15	3.11	2.97	2.55	2.26
2048	3.67	3.66	3.59	3.25	2.84

Temperature Coefficients (Per cent)

v	0-15°	15-25°	25-35°	35-50°	50-65°
32	2.32	1.60	1.32	.98	.69
128	2.25	1.66	1.35	1.04	.71
512	2.36	1.73	1.32	1.02	.79
1024	2.25	1.66	1.36	1.02	.79
2048	2.23	1.67	1.40	1.11	.83

Percentage Dissociation.

v	0°	15°	25°	35°	50°	65°
32	17.11	17.09	16.96	16.83	16.35	15.71
128	31.36	31.08	31.00	30.92	30.35	29.21
512	51.88	52.08	52.25	52.00	50.82	49.48
1024	63.82	63.22	63.05	62.96	61.57	60.00
2048	74.62	73.89	73.48	73.95	73.15	71.65

Dissociation Constants.

v	0°	15°	25°	35°	50°	65°
32	11.0	11.0	10.8	10.6	10.0	9.15
128	11.2	11.0	10.9	10.8	10.3	9.4
512	10.9	11.0	11.1	11.0	10.2	9.5
1024	11.0	10.6	10.5	10.4	9.6	8.8
2048	10.7	10.2	10.0	10.3	9.7	8.8



ALLYLMALONIC ACID.  $\text{CH}_2\text{CH}.\text{CH}_2\text{CH}(\text{COOH})_2$

-:-  
Molecular Conductivity.

v	0°	15°	25°	35°	50°	65°
8	24.25	32.63	37.73	42.26	48.94	53.61
32	45.62	61.58	71.47	80.30	92.02	101.16
128	80.81	109.08	126.33	142.15	164.78	181.65
512	130.5	176.3	204.4	231.0	264.5	293.2
1024	158.9	214.0	248.7	281.0	322.7	358.3
2048	176.4	237.9	277.4	313.8	358.6	401.5

Temperature Coefficients (Cond. units)

v	0-15°	15-25°	25-35°	35-50°	50-65°
8	.56	.51	.45	.44	.31
32	1.06	.99	.88	.78	.61
128	1.88	1.72	1.58	1.51	1.12
512	3.05	2.81	2.66	2.23	1.92
1024	3.67	3.47	3.23	2.78	2.37
2048	4.10	3.95	3.64	2.98	2.86

Temperature Coefficients (Per cent)

v	0-15°	15-25°	25-35°	35-50°	50-65°
8	2.30	1.56	1.20	1.05	.63
32	2.33	1.60	1.23	.98	.66
128	2.33	1.58	1.25	1.06	.68
512	2.33	1.59	1.30	.97	.72
1024	2.31	1.62	1.30	.99	.73
2048	2.32	1.66	1.31	.95	.79

Percentage Dissociation.

v	0	15°	25°	35°	50°	65°
8	10.95	10.90	10.76	10.56	10.46	9.98
32	20.60	20.57	20.37	20.07	19.66	18.84
128	36.49	36.43	36.01	35.54	35.21	33.82
512	58.93	58.87	58.26	57.75	56.52	54.61
1024	71.77	71.47	70.89	70.25	68.96	66.72
2048	79.65	79.45	79.08	78.46	76.62	74.77

Dissociation Constants.

v	0	15°	25°	35°	50°	65°
8	16.8	16.6	16.2	15.6	15.3	13.8
32	16.7	16.6	16.2	15.7	15.0	13.7
128	16.4	16.3	15.8	15.3	14.9	13.5
512	16.5	16.5	15.9	15.4	14.4	12.8
1024	----	----	----	----	14.9	13.1





BENZYL MALONIC ACID.  $C_6H_5CH_2CH(COOH)_2$

Molecular Conductivity.

v	0°	15°	25°	35°	50°	65°
32	45.06	60.54	69.82	78.31	89.05	97.76
128	80.22	107.44	124.99	140.37	160.03	175.82
512	128.3	171.8	199.6	225.1	259.0	285.8
1024	153.0	205.6	239.4	269.6	310.8	345.3
2048	177.7	236.2	273.7	310.0	357.9	395.3

Temperature Coefficients (Cond. units)

v	0-15°	15-25°	25-35°	35-50°	50-65°
32	1.03	.93	.85	.72	.57
128	1.81	1.75	1.54	1.31	1.05
512	2.90	2.78	2.55	2.26	1.79
1024	3.50	3.38	3.02	2.74	2.30
2048	3.89	3.85	3.64	3.19	2.49

Temperature Coefficients (Per cent)

v	0-15°	15-25°	25-35°	35-50°	50-65°
32	2.29	1.53	1.22	.91	.65
128	2.20	1.57	1.23	.93	.66
512	2.29	1.61	1.27	1.00	.69
1024	2.29	1.64	1.26	1.02	.74
2048	2.19	1.63	1.32	1.04	.69

Percentage Dissociation.

v	0°	15°	25°	35°	50°	65°
32	20.57	20.48	20.19	19.91	19.18	18.33
128	36.63	36.34	36.16	35.70	34.49	32.98
512	58.58	58.11	57.74	57.24	55.81	53.62
1024	69.88	69.56	69.26	68.57	66.98	64.79
2048	81.16	79.89	79.16	78.86	77.14	74.16

Dissociation Constants.

v	0°	15°	25°	35°	50°	65°
32	16.6	16.5	16.0	15.5	14.2	12.8
128	16.5	16.2	16.0	15.5	14.1	12.7
512	16.2	15.7	15.4	15.0	13.8	12.1
1024	15.8	15.5	15.2	14.6	13.3	11.7
2048	17.0	15.5	14.7	14.4	12.7	10.4



DIMETHYLMALONIC ACID.  $(\text{CH}_3)_2\text{C}(\text{COOH})_2$

Molecular Conductivity.

v	0°	15°	25°	35°	50°	65°
8	16.08	22.06	25.83	29.27	34.10	38.13
32	32.00	43.76	51.23	58.41	68.80	77.10
128	59.00	80.57	94.61	107.29	124.82	139.53
512	101.4	136.9	160.3	182.5	217.2	240.7
1024	124.1	169.7	198.9	226.0	266.7	299.3
2048	151.9	205.7	241.1	273.7	314.71	349.5

Temperature Coefficients (Cond. units)

v	0-15°	15-25°	25-35°	35-50°	50-65°
8	.40	.38	.34	.32	.27
32	.78	.75	.72	.69	.55
128	1.44	1.40	1.27	1.17	.98
512	2.37	2.33	2.22	2.13	1.57
1024	3.04	2.92	2.71	2.71	2.17
2048	3.59	3.54	3.26	2.74	2.32

Temperature Coefficients (Per cent)

v	0-15°	15-25°	25-35°	35-50°	50-65°
8	2.44	1.70	1.34	1.08	.79
32	2.43	1.70	1.40	1.18	.80
128	2.42	1.74	1.34	1.09	.79
512	2.33	1.70	1.38	1.17	.72
1024	2.45	1.72	1.36	1.18	.82
2048	2.36	1.72	1.35	1.00	.74

Percentage Dissociation.

v	0°	15°	25°	35°	50°	65°
8	7.24	7.35	7.34	7.32	7.25	7.07
32	14.40	14.59	14.56	14.62	14.63	14.30
128	26.55	26.86	26.89	26.85	26.56	25.88
512	45.64	45.65	45.56	45.66	46.17	44.66
1024	55.85	56.58	56.55	56.56	56.72	55.52
2048	68.36	68.57	68.53	68.48	67.00	64.85

Dissociation Constants.

v	0°	15°	25°	35°	50°	65°
8	7.06	7.28	7.27	7.27	7.08	6.72
32	7.57	7.79	7.75	7.82	7.82	7.45
128	7.50	7.71	7.73	7.70	7.51	7.06
512	7.48	7.49	7.45	7.50	7.69	7.04
1024	6.90	7.20	7.21	7.20	7.26	6.77
2048	7.21	7.30	7.29	7.28	6.64	5.84



Molecular Conductivity.

v	0°	15°	25°	35°	50°	65°
8	23.60	31.90	37.34	42.22	48.28	54.11
32	45.89	61.89	72.45	82.00	93.61	104.35
128	81.39	110.44	129.71	147.18	168.51	188.20
512	129.9	176.0	206.3	234.0	269.5	304.3
1024	156.2	211.2	248.2	280.0	323.2	365.5
2048	178.2	240.3	280.6	315.1	365.5	411.6

Temperature Coefficients (Cond. units)

v	0-15°	15-25°	25-35°	35-50°	50-65°
8	.55	.54	.49	.40	.39
32	1.07	1.06	.95	.77	.72
128	1.94	1.93	1.75	1.42	1.31
512	3.07	3.04	2.77	2.37	2.32
1024	3.67	3.69	3.18	2.88	2.82
2048	4.14	4.03	3.44	3.36	3.07

Temperature Coefficients (Per cent)

v	0-15°	15-25°	25-35°	35-50°	50-65°
8	2.34	1.70	1.30	.96	.72
32	2.33	1.71	1.31	.94	.76
128	2.38	1.74	1.34	.96	.77
512	2.36	1.72	1.34	1.01	.85
1024	2.35	1.75	1.28	1.02	.87
2048	2.32	1.70	1.23	1.07	.83

Percentage Dissociation.

v	0°	15°	25°	35°	50°	65°
8	10.68	10.67	10.67	10.61	10.39	10.15
32	20.78	20.70	20.71	20.61	20.17	19.58
128	36.85	36.94	37.08	36.99	36.31	35.31
512	58.84	58.85	58.99	58.81	58.08	57.08
1024	70.73	70.66	70.96	70.37	69.65	68.58
2048	80.68	80.38	80.25	79.18	78.76	77.22

Dissociation Constants.

v	0°	15°	25°	35°	50°	65°
8	16.0	15.9	15.9	15.7	15.6	14.3
32	17.0	16.9	16.9	16.7	15.9	14.5
128	16.8	16.9	17.1	17.0	16.1	15.0
512	16.4	16.4	16.6	16.4	15.7	14.8
1024	16.7	16.6	16.9	16.3	15.6	14.6
2048	16.5	16.1	15.9	15.0	14.3	12.8



DIETHYLMALONIC ACID.  $(C_2H_5)_2C(COOH)_2$

:-  
Molecular Conductivity.

v	0°	15°	25°	35°	50°	65°
8	52.38	67.87	76.92	84.66	94.03	100.32
32	92.77	121.64	138.84	153.60	174.26	186.22
128	141.8	187.3	215.3	240.2	275.0	299.0
512	189.0	252.3	292.2	328.7	378.8	422.6
1024	201.2	268.2	312.0	353.6	413.7	462.9
2048	201.6	272.2	317.2	360.5	424.4	471.6

Temperature Coefficients (Cond. units)

v	0-15°	15-25°	25-35°	35-50°	50-65°
8	1.03	.90	.77	.72	.42
32	1.92	1.72	1.48	1.38	.80
128	3.04	2.80	2.49	2.33	1.67
512	4.22	3.99	3.65	3.34	2.92
1024	4.47	4.37	4.16	4.01	3.27
2048	4.71	4.50	4.32	4.26	3.83

Temperature Coefficients (Per cent)

v	0-15°	15-25°	25-35°	35-50°	50-65°
8	1.97	1.33	1.00	.85	.44
32	2.07	1.41	1.06	.89	.46
128	2.14	1.49	1.15	.97	.61
512	2.23	1.58	1.25	1.01	.77
1024	2.22	1.63	1.33	1.13	.79
2048	2.33	1.65	1.36	1.18	.90

Percentage Dissociation.

v	0°	15°	25°	35°	50°	65°
8	23.88	22.92	22.22	21.49	20.23	18.79
32	42.29	41.08	40.10	39.00	37.49	34.87
128	64.65	63.27	62.19	60.98	59.15	56.00
512	86.17	85.21	84.40	83.46	81.56	79.14
1024	91.73	90.59	90.10	89.76	89.00	86.66
2048	91.92	91.94	91.62	91.52	91.30	88.32





DIPROPYLMALONIC ACID.  $(C_3H_7)_2C(COOH)_2$ .-:-  
Molecular Conductivity.

v.	0°	15°	25°	35°	50°	65°
32	107.2	135.1	154.5	170.3	-----	-----
128	152.2	204.4	234.9	261.7	297.5	304.2
512	192.1	258.8	300.6	339.3	386.5	430.1
1024	203.5	272.9	317.8	359.1	417.0	468.0
2048	209.3	281.1	328.9	373.0	434.6	490.9

## Temperature Coefficients (Cond. units)

v	0-15°	15-25°	25-35°	35-50°	50-65°
32	2.13	1.94	1.58	-----	-----
128	3.47	3.06	2.68	2.39	1.78
512	4.45	4.18	3.86	3.15	2.95
1024	4.63	4.49	4.14	3.86	3.40
2048	4.78	4.78	4.41	4.11	3.75

## Temperature Coefficients (Per cent)

v	0-15°	15-25°	25-35°	35-50°	50-65°
32	2.06	1.41	1.02	-----	-----
128	2.28	1.49	1.14	.91	.60
512	2.31	1.62	1.28	.93	.74
1024	2.27	1.64	1.30	1.09	.81
2048	2.29	1.70	1.34	1.10	.86

## Percentage Dissociation.

v	0°	15°	25°	35°	50°	65°
32	47.18	45.78	44.70	43.35	-----	-----
128	69.63	69.25	67.95	66.60	64.96	62.34
512	87.85	87.70	86.97	86.35	84.40	82.77
1024	93.07	92.48	91.92	91.41	91.06	90.00
2048	95.74	95.26	95.15	94.93	94.89	94.40

## Dissociation Constants.

v	0°	15°	25°	35°	50°	65°
32	132	121	113	104	-----	-----
128	125	121	113	104	90	81
512	124	122	113	106	89	78
1024	122	111	102	95	90	79
2048	105	93	91	90	90	78



BROMOSUCCINIC ACID.  $\text{COOH.CHBr.CHH.COOH}$ -:-  
Molecular Conductivity.

v	0°	15°	25°
128	101.46	136.01	158.19
512	156.00	210.27	246.72
1024	189.44	252.44	293.74
2048	208.37	283.02	328.50

## Temperature Coefficients (Cond. units)

v	0-15°	15-25°
128	2.30	2.21
512	3.62	3.60
1024	4.20	4.13
2048	4.71	4.55

## Temperature Coefficients (Per cent)

v	0-15°	15-25°
128	2.27	1.60
512	2.32	1.62
1024	2.22	1.60
2048	2.26	1.61

## Percentage Dissociation.

v	0°	15°	25°
128	45.66	45.02	44.67
512	70.20	70.40	69.66
1024	85.25	83.55	82.94
2048	93.77	93.67	92.76

## Dissociation Constants.

v	0°	15°	25°
128	30	29	28
512	32	33	31
1024	48	41	39
2048	69	68	58



DIBROMSUCGINIC ACID.  $\text{COOH} \cdot \text{CHBr} \cdot \text{CHBr} \cdot \text{COOH}$ .-:-  
Molecular Conductivity.

v	0°	15°	25°	35°	50°	65°
32	175.6	222.2	245.6	262.9	293.4	342.6
128	254.3	326.8	367.6	399.7	448.6	509.8
512	339.1	438.4	497.4	546.5	615.6	685.9
1024	381.6	501.8	571.4	635.0	707.1	786.1
2048	416.1	550.0	631.9	704.9	792.2	879.4

## Temperature Coefficients (Cond. units)

v	0-15°	15-25°	25-35°	35-50°	50-65°
32	3.10	2.34	1.74	2.03	3.28
128	4.83	4.07	3.21	3.26	4.08
512	6.62	5.99	4.91	4.56	4.73
1024	8.01	6.96	6.35	4.81	5.26
2048	8.93	8.19	7.39	5.82	5.82

## Temperature Coefficients (Per cent)

v	0-15°	15-25°	25-35°	35-50°	50-65°
32	1.77	1.05	.71	.77	1.09
128	1.89	1.24	.87	.82	.91
512	1.95	1.34	.98	.83	.77
1024	2.10	1.39	1.11	.76	.74
2048	2.14	1.49	1.15	.83	.73



PYROMUGIC ACID.  $C_4H_3O.COOH.$ 

-:-

## Molecular Conductivity.

v	35°	50°	65°
8	28.59	31.59	33.36
32	56.36	62.36	66.56
128	105.01	116.32	124.38
512	179.4	199.9	213.8
1024	223.0	249.2	265.3
2048	269.2	308.9	333.9

## Temperature Coefficients (Cond. units)

v	35-50°	50-65°
8	.20	.12
32	.40	.28
128	.75	.54
512	1.37	.93
1024	1.78	1.07
2048	2.65	1.67

## Temperature Coefficients (Per cent)

v	35-50°	50-65°
8	.70	.37
32	.71	.45
128	.72	.46
512	.76	.46
1024	.79	.43
2048	.98	.54

## Percentage Dissociation.

v	35°	50°	65°
8	7.07	6.71	6.19
32	13.93	13.24	12.34
128	25.96	24.69	23.07
512	44.35	42.44	39.65
1024	55.13	52.91	49.20
2048	66.55	65.58	61.93

## Dissociation Constants.

v	35°	50°	65°
8	6.7	6.0	5.1
32	7.0	6.3	5.4
128	7.1	6.3	5.4
512	6.9	6.1	5.1
1024	6.6	5.8	4.8
2048	6.5	6.1	4.9





PHENYLPROPIOLIC ACID.  $C_6H_5C:C.COOH$ .

-:-

Molecular Conductivity.

v	0°	15°	25°	35°	50°	65°
128	132.6	177.0	203.3	227.2	255.6	274.7
256	154.8	208.0	239.2	267.6	301.2	327.4
512	176.1	236.6	274.4	307.8	349.7	375.3
1024	191.4	258.0	299.8	339.2	392.1	422.1
2048	200.5	269.0	314.8	357.9	416.6	449.6

Temperature Coefficients (Cond. units)

v	0-15°	15-25°	25-35°	35-50°	50-65°
128	2.96	2.63	2.39	1.89	1.27
256	3.54	3.12	2.84	2.24	1.53
512	4.05	3.78	3.34	2.77	1.71
1024	4.44	4.08	3.94	3.53	2.00
2048	4.56	4.58	4.31	3.91	2.20

Temperature Coefficients (Per cent)

v	0-15°	15-25°	25-35°	35-50°	50-65°
128	2.23	1.48	1.17	.83	.50
256	2.24	1.50	1.18	.84	.51
512	2.25	1.59	1.21	.90	.49
1024	2.32	1.62	1.31	1.04	.51
2048	2.27	1.70	1.36	1.09	.53

Percentage Dissociation.

v	0°	15°	25°	35°	50°	65°
128	59.67	58.91	57.87	56.82	54.39	50.98
256	69.66	69.22	68.08	66.90	64.09	60.76
512	79.24	78.76	78.12	76.97	74.41	69.66
1024	86.15	85.89	85.34	84.81	83.43	78.35
2048	90.25	89.54	89.60	89.48	88.63	83.43

Dissociation Constants.

v	0°	15°	25°	35°	50°	65°
128	68.9	66.0	62.1	58.4	50.7	41.4
256	62.5	60.8	56.7	52.8	44.7	36.8
512	59.1	57.0	54.5	50.2	42.3	31.2
1024	52.3	51.1	48.5	46.2	41.0	27.7
2048	40.8	37.4	37.7	37.2	33.7	20.5



SALICYLICACID. (OH)C<sub>6</sub>H<sub>4</sub>COOH.

-:-

## Molecular Conductivity.

v	35°	50°	65°
64	93.64	110.55	124.60
128	125.96	148.72	166.80
512	209.7	249.1	280.1
1024	255.0	301.7	337.2
2048	294.6	350.1	392.6

## Temperature Coefficients (Cond. Units)

v	35-50°	50-65°
64	1.13	.94
128	1.52	1.20
512	2.63	2.07
1024	3.11	2.37
2048	3.70	2.77

## Temperature Coefficients (Per cent)

v	35-50°	50-65°
64	1.21	.85
128	1.21	.81
512	1.25	.83
1024	1.22	.79
2048	1.25	.79

## Percentage Dissociation.

v	35°	50°	65°
64	23.24	23.37	23.13
128	31.26	31.44	30.96
512	52.05	52.67	52.00
1024	63.29	63.78	62.58
2048	73.12	74.01	72.87

## Dissociation Constants.

v	35°	50°	65°
64	11.0	11.1	10.9
128	11.1	11.2	10.8
512	11.0	11.4	11.0
1024	10.7	11.0	10.2



ACETYLSALICYLIC ACID.  $(\text{CH}_3\text{CO.O})\text{C}_6\text{H}_4\text{COOH}$ .

-:-

## Molecular Conductivity.

v	0°	15°	25°	35°	50°
128	40.40	52.78	60.60	68.89	79.41
512	73.10	95.21	109.27	124.34	142.88
1024	92.60	121.0	139.3	158.7	184.1
2048	118.1	154.5	177.6	205.1	238.3

## Temperature Coefficients (Cond. units)

v	0-15°	15-25°	25-35°	35-50°
128	.83	.78	.83	.70
512	1.47	1.41	1.51	1.24
1024	1.89	1.83	1.94	1.69
2048	2.43	2.30	2.75	2.35

## Temperature Coefficients (Per cent)

v	0-15°	15-25°	25-35°	35-50°
128	2.04	1.48	1.37	1.02
512	2.01	1.48	1.38	1.00
1024	2.04	1.51	1.39	1.06
2048	2.14	1.49	1.54	1.14

## Percentage Dissociation.

v	0°	15°	25°	35°	50°
128	18.30	17.75	17.59	17.31	17.13
512	33.11	32.00	31.73	31.25	30.82
1024	41.49	40.68	40.45	39.89	39.72
2048	53.50	51.95	51.55	51.54	51.42

## Dissociation Constants.

v	0°	15°	25°	35°	50°
128	3.2	3.0	2.9	2.8	2.7
512	3.2	2.9	2.9	2.8	2.7
1024	3.0	2.7	2.7	2.6	2.6
2048	3.0	2.7	2.7	2.7	2.7



SULPHOSALICYLIC ACID.  $\text{OH.C}_6\text{H}_3(\text{SO}_3\text{H})\text{COOH}$ .

-:-

## Molecular Conductivity.

v	0°	15°	25°	35°	50°	65°
32	209.4	283.7	332.0	377.6	432.9	486.8
128	239.6	328.5	386.5	440.1	508.9	575.4
512	291.9	403.3	474.1	538.5	622.4	706.2
1024	322.5	443.0	522.4	598.1	701.3	785.7
2048	352.0	485.0	570.4	651.7	762.3	858.0

## Temperature Coefficients (Cond. units)

v	0-15°	15-25°	25-35°	35-50°	50-65°
32	4.95	4.83	4.56	3.69	3.59
128	5.93	5.79	5.36	4.61	4.43
512	7.42	7.08	6.44	5.59	5.58
1024	8.04	7.93	7.57	6.84	5.62
2048	8.87	8.54	8.13	7.38	6.38

## Temperature Coefficients (Per cent)

v	0-15°	15-25°	25-35°	35-50°	50-65°
32	2.36	1.70	1.37	.98	.83
128	2.47	1.76	1.38	1.05	.87
512	2.54	1.75	1.35	1.04	.89
1024	2.49	1.79	1.44	1.14	.81
2048	2.51	1.76	1.42	1.13	.84





ANISIC ACID.  $\text{CH}_3\text{O.C}_6\text{H}_4\text{COOH}$ .-:-  
Molecular Conductivity.

v	0°	15°	25°	35°	50°	65°
1024	35.80	50.50	59.10	67.60	80.29	90.25
2048	47.13	66.74	78.80	90.15	103.67	115.17

## Temperature Coefficients (Cond. units)

v	0-15°	15-25°	25-35°	35-50°	50-65°
1024	.98	.86	.85	.84	.66
2048	1.31	1.20	1.13	.90	.77

## Temperature Coefficients (Per cent)

v	0-15°	15-25°	25-35°	35-50°	50-65°
1024	2.74	1.70	1.43	1.24	.82
2048	2.77	1.80	1.43	1.00	.74

## Percentage Dissociation.

v	0°	15°	25°	35°	50°	65°
1024	16.14	16.84	16.88	16.94	17.06	16.80
2048	21.26	22.25	22.50	22.59	22.63	21.44

## Dissociation Constants.

v	0°	15°	25°	35°	50°	65°
1024	.303	.333	.335	.337	.343	.331
2048	.280	.311	.319	.322	.304	.285



VANILLIC ACID.  $\text{CH}_3\text{O.C}_6\text{H}_3(\text{HO})\text{COOH}$ .

Molecular Conductivity.

v	0°	15°	25°	35°	50°	65°
256	18.48	26.44	31.68	36.49	42.32	47.41
512	26.16	36.65	43.30	49.89	57.80	64.62
1024	35.87	50.10	59.55	69.00	80.38	89.42
2048	47.26	67.40	80.88	93.48	109.15	120.08

Temperature Coefficients (Cond. units)

v	0-15°	15-25°	25-35°	35-50°	50-65°
256	.53	.52	.48	.39	.34
512	.70	.66	.66	.53	.45
1024	.95	.95	.94	.76	.60
2048	1.34	1.34	1.26	1.04	.73

Temperature Coefficients (Per cent)

v	0-15°	15-25°	25-35°	35-50°	50-65°
256	2.87	1.98	1.52	1.07	.80
512	2.67	1.81	1.52	1.06	.79
1024	2.63	1.88	1.58	1.10	.75
2048	2.80	1.99	1.55	1.11	.67

Percentage Dissociation.

v	0°	15°	25°	35°	50°	65°
256	8.35	8.84	9.05	9.18	9.12	8.90
512	11.82	12.25	12.38	12.56	12.46	12.13
1024	16.21	16.75	17.33	17.37	17.32	16.78
2048	21.35	22.53	23.12	23.53	23.52	22.54

Dissociation Constants.

v	0°	15°	25°	35°	50°	65°
256	.30	.33	.35	.36	.36	.34
512	.31	.33	.34	.35	.35	.33
1024	.31	.33	.35	.36	.35	.33
2048	.28	.32	.34	.35	.35	.32



METANILIC ACID.  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{H}$

Molecular Conductivity.

v	35°	50°	65°
32	35.37	49.48	66.05
128	66.86	92.74	123.89
512	122.35	165.15	216.84
1024	158.2	210.0	267.3
2048	202.4	264.3	331.7

Temperature Coefficients (Cond. units)

v	35-50°	50-65°
32	.94	1.10
128	1.72	2.08
512	2.85	3.44
1024	3.45	3.82
2048	4.13	4.49

Temperature Coefficients (Per cent)

v	35-50°	50-65°
32	2.66	2.23
128	2.57	2.24
512	2.33	2.09
1024	2.18	1.81
2048	2.04	1.63

Percentage Dissociation.

v	35°	50°	65°
32	8.84	10.53	12.25
128	16.72	19.73	22.99
512	30.58	35.14	40.24
1024	39.55	44.68	49.61
2048	50.60	56.23	61.56

Dissociation Constants.

v	35°	50°	65°
32	2.68	3.87	5.34
128	2.62	3.80	5.36
512	2.63	3.72	5.29
1024	2.53	3.52	4.79
2048	2.53	3.53	4.81



SULPHANILICACID.  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{H}$   
 :-

Molecular Conductivity.

v	25°	35°	50°	65°
32	45.39	58.35	78.23	100.50
128	85.40	107.80	145.00	186.40
512	148.66	180.88	237.00	298.00
1024	182.8	221.6	287.0	352.6
2048	223.0	268.0	336.8	406.7

Temperature Coefficients (Cond. units)

v	25-35°	35-50°	50-65°
32	1.30	1.33	1.48
128	2.24	2.48	2.73
512	3.22	3.73	4.07
1024	3.88	4.36	4.37
2048	4.50	4.58	4.66

Temperature Coefficients (Per cent)

v	25-35°	35-50°	50-65°
32	2.68	2.28	1.89
128	2.62	2.30	1.88
512	2.17	2.06	1.72
1024	2.12	1.97	1.52
2048	2.02	1.71	1.38

Percentage Dissociation.

v	25°	35°	50°	65°
32	12.94	14.59	16.64	18.65
128	24.34	26.95	30.85	34.59
512	41.79	45.22	50.42	55.30
1024	52.08	55.40	61.06	65.44
2048	63.52	67.00	71.65	75.48

Dissociation Constants.

v	25°	35°	50°	65°
32	6.01	7.78	10.4	13.4
128	6.09	7.77	10.7	14.2
512	5.86	7.30	10.0	13.4
1024	5.53	6.72	9.35	12.1
2048	5.40	6.64	8.84	11.3





4.6. DINITRO 2. AMINO PHENOL.  $C_6H_3(NO_2)_2NH_2.OH$   
-:-

Molecular Conductivity.

v	0°	15°	25°	35°	50°	65°
512	24.00	39.78	51.80	64.93	85.67	110.8
1024	32.90	54.09	70.16	88.60	119.00	153.5
2048	44.60	73.80	95.20	119.7	161.8	208.4

Temperature Coefficients (Cond. units)

v	0-15°	15-25°	25-35°	35-50°	50-65°
512	1.05	1.20	1.31	1.38	1.67
1024	1.41	1.61	1.84	2.02	2.30
2048	1.95	2.26	2.45	2.80	3.11

Temperature Coefficients (Per cent)

v	0-15°	15-25°	25-35°	35-50°	50-65°
512	4.37	3.02	2.53	2.12	1.94
1024	4.30	2.97	2.58	2.28	1.93
2048	4.37	3.10	2.57	2.34	1.92

Percentage Dissociation.

v	0°	15°	25°	35°	50°	65°
512	10.82	13.30	14.73	16.27	18.22	20.62
1024	14.84	18.08	19.95	22.20	25.32	28.57
2048	20.10	24.61	27.20	29.93	34.42	38.79

Dissociation Constants.

v	0°	15°	25°	35°	50°	65°
512	.256	.398	.497	.617	.793	1.05
1024	.253	.389	.486	.619	.838	1.11
2048	.247	.392	.496	.624	.882	1.20



HYDROCINNAMIC ACID.  $C_6H_5.CH_2.CH_2.COOH$

--

Molecular Conductivity.

$\nu$	0°	15°	25°	35°	50°	65°
32	5.89	8.07	9.40	10.57	11.81	13.00
128	11.49	15.64	18.32	20.56	23.20	25.28
512	22.18	30.46	35.49	39.85	44.82	49.00
1024	30.40	41.76	48.84	54.79	61.37	67.04
2048	41.60	56.41	65.65	73.72	83.02	89.66

Temperature Coefficients (Cond. units)

$\nu$	0-15°	15-25°	25-35°	35-50°	50-65°
32	.145	.133	.104	.083	.079
128	.276	.268	.224	.176	.138
512	.552	.503	.436	.331	.278
1024	.757	.708	.595	.438	.378
2048	.987	.924	.807	.62	.443

Temperature Coefficients (Per cent)

$\nu$	0-15°	15-25°	25-35°	35-50°	50-65°
32	2.47	1.65	1.24	.78	.67
128	2.41	1.71	1.22	.85	.59
512	2.49	1.65	1.23	.83	.62
1024	2.49	1.69	1.22	.80	.61
2048	2.37	1.64	1.23	.84	.53

Percentage Dissociation.

$\nu$	0°	15°	25°	35°	50°	65°
32	2.67	2.70	2.69	2.66	2.55	2.44
128	5.20	5.23	5.23	5.17	5.01	4.75
512	10.04	10.17	10.14	10.03	9.67	9.20
1024	13.76	13.97	13.96	13.79	13.24	12.59
2048	18.84	18.87	18.77	18.56	17.91	16.83

Dissociation Constants.

$\nu$	0°	15°	25°	35°	50°	65°
32	.229	.234	.232	.227	.208	.191
128	.223	.225	.225	.220	.206	.185
512	.219	.225	.223	.218	.202	.182
1024	.214	.222	.221	.215	.197	.177
2048	.214	.214	.212	.205	.191	.166



CINNAMIC ACID.  $\text{C}_6\text{H}_5\text{CH}:\text{CH}.\text{COOH}$   
 -:-

Molecular Conductivity.

v	35°	50°	65°
512	51.10	59.90	67.02
1024	69.40	80.93	90.20
2048	95.25	111.00	124.00

Temperature Coefficients (Cond. units)

v	35-50°	50-65°
512	.58	.47
1024	.77	.62
2048	1.05	.87

Temperature Coefficients (Per cent)

v	35-50°	50-65°
512	1.13	.79
1024	1.11	.77
2048	1.10	.78

Percentage Dissociation.

v	35°	50°	65°
512	12.80	12.74	12.48
1024	17.38	17.22	16.79
2048	23.86	23.62	23.08

Dissociation Constants.

v	35°	50°	65°
512	.367	.363	.347
1024	.357	.350	.331
2048	.365	.357	.338



(o) COUMARIC ACID.  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CH} \cdot \text{COOH}.$   
 -:-

Molecular Conductivity.

v	0°	15°	25°	35°	50°	65°
256	16.00	23.22	27.08	30.38	35.56	39.39
512	22.40	32.39	37.58	42.01	49.08	54.24
1024	31.48	46.00	53.38	59.52	69.57	76.92
2048	44.53	65.13	75.56	77.50	90.50	98.75

Temperature Coefficients (Cond. units)

v	0-15°	15-25°	25-35°	35-50°	50-65°
256	.48	.38	.33	.34	.25
512	.67	.52	.44	.47	.34
1024	.97	.74	.61	.67	.49
2048	1.38	1.04	.19	.87	.55

Temperature Coefficients (Per cent)

v	0-15°	15-25°	25-35°	35-50°	50-65°
256	3.00	1.64	1.21	1.13	.71
512	2.99	1.61	1.18	1.12	.70
1024	3.07	1.63	1.15	1.12	.70
2048	3.08	1.60	0.25	1.12	.61

Percentage Dissociation.

v	0°	15°	25°	35°	50°	65°
256	7.27	7.74	7.73	7.60	7.59	7.37
512	10.18	10.80	10.74	10.51	10.48	10.15
1024	14.30	15.34	15.25	14.89	14.86	14.39
2048	20.23	21.72	21.59	19.39	19.34	18.48

Dissociation Constants.

v	0°	15°	25°	35°	50°	65°
256	.223	.254	.253	.244	.243	.229
512	.225	.255	.252	.241	.240	.224
1024	.233	.271	.268	.254	.252	.236
2048	.250	.294	.290	.228	.226	.205





(o) PHTHALIC ACID.  $C_6H_4(COOH)_2$   
 -:-

Molecular Conductivity.

v	35°	50°	65°
64	96.31	110.20	122.70
128	128.06	147.58	163.86
512	212.8	244.8	272.4
1024	258.5	300.3	336.9
2048	302.7	352.7	395.1

Temperature Coefficients (Cond. units)

v	35-50°	50-65°
64	.93	.83
128	1.30	1.09
512	2.13	1.84
1024	2.78	2.44
2048	3.33	2.83

Temperature Coefficients (Per cent)

	35-50°	50-65°
64	.96	.75
128	1.02	.74
512	1.01	.75
1024	1.08	.81
2048	1.10	.80

Percentage Dissociation.

v	35°	50°	65°
64	24.08	23.45	22.77
128	32.01	31.40	30.41
512	53.20	52.09	50.55
1024	64.62	63.89	62.53
2048	75.68	75.04	73.33

Dissociation Constants.

v	35°	50°	65°
64	11.9	11.2	10.5
128	11.8	11.2	10.4
512	11.8	11.1	10.1
1024	11.5	11.0	10.2
2048	11.5	11.0	9.8



NAPHTHIONIC ACID.  $C_{10}H_6(NH_2).SO_3H$   
 :-

Molecular Conductivity.

v	0°	15°	25°	35°	50°	65°
1024	142.2	212.7	262.0	312.9	382.6	450.6
2048	169.8	245.5	295.4	347.2	420.9	491.2

Temperature Coefficients (Cond. units)

v	0-15°	15-25°	25-35°	35-50°	50-65°
1024	4.70	4.93	5.09	4.64	4.56
2048	5.05	4.99	5.16	4.92	4.68

Temperature Coefficients (Per cent)

v	0-15°	15-25°	25-35°	35-50°	50-65°
1024	3.30	2.32	1.94	1.48	1.19
2048	3.00	2.03	1.48	1.42	1.11

Percentage Dissociation.

v	0°	15°	25°	35°	50°	65°
1024	64.04	71.82	74.43	78.23	81.75	84.29
2048	76.58	82.98	83.92	86.80	89.94	91.90

Dissociation Constants.

v	0°	15°	25°	35°	50°	65°
1024	11.1	17.9	21.2	27.4	35.8	44.2
2048	12.2	19.7	21.4	27.9	39.3	50.9



The conductivities of bromsuccinic and acetylsalicylic acids could not be measured at higher temperatures. Both acids showed marked evidence of decomposition.

The time factor for the decomposition of bromsuccinic acid is striking.

$\eta$	time	$M_v$ 35°
1024	30 minutes	442
	45 "	458
	1 hour	466
	1 1/2 "	472

Acetylsalicylic acid in all probability gives salicylic and acetic acids as a result of hydrolysis.



The velocity of this reaction may be observed in the following data:

$\eta$	time	$M_v$ 65°
128	35 minutes	93.8
	45 "	94.9
	1 hour, 10 minutes	97.3
	2 " 15 "	105.8
	3 "	111.0



Possibly the weakening action of the substituting acetyl group in this acid finds its explanation here. We would expect acetyl salicylic acid, under ordinary conditions, to be stronger than salicylic acid. The acetyl derivatives of propionic (1) and amido benzoic (2) acids are stronger than the original unsubstituted acids. Since, however, acetylsalicylic acid shows such marked evidence of hydrolysis, we think it fair to assume that its small conductivity is due to its great hydrating power.

The  $\mu_{\infty}$  values for sulphosalicylic and dibromsuccinic acids, as has already been explained in connection with the table of limiting conductivities, could not be calculated. Therefore, the percentage dissociation and dissociation constants for these acids are not given.

The case of diethylmalonic acid is exceptional. The molecular conductivities at  $v. = 1024$  and  $v. = 2048$  are so nearly alike that we might imagine the acid to be almost completely dissociated at these dilutions. Calculated in the usual manner, however, the  $\mu_{\infty}$  values do not agree with these. Take for example,  $\mu_{\infty}$  at  $0^{\circ}$ . For an acid with 23 atoms the

$\mu_{\infty} = 219.4$ . In the case of diethylmalonic acid the experimentally obtained  $\mu_{\infty} = 201.6$ . Dissociation constants calculated on the basis of the theoretical  $\mu_{\infty}$  scarcely deserve the name of "constants", and are therefore omitted from our list.

Owing to the fact that the Ostwald dilution law does not

---

(1) Am. Chem. J., 46, 78

(2) Z. physik chem. 3, 263.





hold for strong acids, many "dissociation constants" belonging to acids of this class are omitted. Some that are given are extremely irregular and are only of value inasmuch as they indicate the relative strengths of the acids.

In the following table are the probable dissociation constants of most of the acids with which we worked.

DISSOCIATION CONSTANTS		K $10^4$				
		-:-				
Acid	0°	15°	25°	35°	50°	65°
Phenylacetic	0.540*	-----	0.545*	0.506	0.477	0.416
Ethylmalonic	12.5	12.4	12.3	11.9	11.0	10.0
Isopropylmalonic	12.3	12.5	13.2	12.9	12.5	11.3
Butyl malonic	11.0	10.9	10.8	10.6	10.2	9.4
Allyl malonic	16.6	16.5	16.0	15.5	14.9	13.4
Benzyl malonic	16.4	15.9	15.5	15.0	13.6	12.0
Dimethylmalonic	7.29	7.46	7.45	7.46	7.33	7.01
Methyl ethyl malonic	16.6	16.5	16.5	16.2	15.8	14.6
Diethyl malonic	88	80	74	69	60	50
Dipropylmalonic	124	121	113	104	90	79
Pyromucic	8.7*	-----	7.6*	6.8	6.1	5.1
Salicylic	8.3*	-----	10.6*	10.9	11.2	10.7
Acetylsalicylic	3.10	2.82	2.80	2.72	2.67	----
Anisic	0.291	0.322	0.327	0.330	0.324	0.308
Vanillic	0.300	0.330	0.345	0.355	0.353	0.330
Metanilic	0.90*	-----	1.99*	2.64	3.80	5.33
Sulphanilic	3.28*	-----	6.05	7.77	10.4	13.4
Dinitro-amino- phenol	0.252	0.393	0.493	0.62	0.84	1.12
Hydro-cinnamic	0.220	0.224	0.223	0.217	0.206	0.186
Cinnamic	0.322*	-----	0.368*	0.363	0.357	0.339
Coumaric	0.233	0.269	0.266	0.242	0.240	0.224
Phthalic	13.4*	-----	12.6*	11.7	11.1	10.2
Naphthionic	11.7	18.8	21.3	27.6	37.5	47.5

\*These constants at lower temperatures were calculated by White and Jones, Am. Chem. J. 44, 159 (1910)

THESE DOCUMENTS ARE THE PROPERTY OF THE NATIONAL ARCHIVES

REPRODUCTION OF THESE DOCUMENTS IS PROHIBITED

EXCEPT BY THE NATIONAL ARCHIVES

Date	Nom	Prénoms	Lieu de naissance	Date de naissance	Date de décès	Remarques
1870	...	...	...	...	...	...
1871	...	...	...	...	...	...
1872	...	...	...	...	...	...
1873	...	...	...	...	...	...
1874	...	...	...	...	...	...
1875	...	...	...	...	...	...
1876	...	...	...	...	...	...
1877	...	...	...	...	...	...
1878	...	...	...	...	...	...
1879	...	...	...	...	...	...
1880	...	...	...	...	...	...
1881	...	...	...	...	...	...
1882	...	...	...	...	...	...
1883	...	...	...	...	...	...
1884	...	...	...	...	...	...
1885	...	...	...	...	...	...
1886	...	...	...	...	...	...
1887	...	...	...	...	...	...
1888	...	...	...	...	...	...
1889	...	...	...	...	...	...
1890	...	...	...	...	...	...
1891	...	...	...	...	...	...
1892	...	...	...	...	...	...
1893	...	...	...	...	...	...
1894	...	...	...	...	...	...
1895	...	...	...	...	...	...
1896	...	...	...	...	...	...
1897	...	...	...	...	...	...
1898	...	...	...	...	...	...
1899	...	...	...	...	...	...
1900	...	...	...	...	...	...

Fin

Several investigators, who had not made measurements at such high temperatures, observed that while most of the percentage dissociations of organic acids decreased with rising temperature, some of them persistently increased. This increase, however, continued at a diminishing rate. The maximum dissociation has been reached in our work in every case except for the amino acids--sulphanitic, metanilic, naphthionic, dinitro aminophenol. The next class of acids for which the dissociation increased over a wide range of temperature were those acids related to hydroxy benzoic--salicylic, anisic, and vanillic acids. These attained maximum dissociation at 35°.

The above mentioned amino acids obey the observations of White and Jones. Their percentage temperature coefficients of conductivity are exceptionally large, and the coefficients expressed in conductivity units increase with rise in temperature. The dissociation constants of dinitro amino-phenol and naphthionic acid also increase slightly with dilution. Ostwald <sup>(1)</sup> has accounted for all these facts by assuming that at low temperatures and high concentration these amino acids form inner salts, which break down on increasing the temperature or the dilution or both, yielding the free acid. This acid conducts better than the salt itself. In other words, conductivity rises exceptionally rapidly with temperature and dilution. Walker <sup>(2)</sup> has also advanced a theory accounting for the increase of the "constants" with dilution. Since our data do not exhibit this phenomenon to any striking degree, a lengthy discussion of his article here would be superfluous. Briefly, he says that these amino acids are amphoteric

(1) Z physik. Chem., 3, 261 (1889)

(2) Ibid., 49, 82 (1904)



electrolytes, and have two dissociation constants, corresponding to dissociation into acid and base.

Probably the nicest example of decreasing dissociation with rise in temperature is found in the case of dichloroacetic acid--a typical strong acid. This attains maximum dissociation at  $v = 1024$  at the lower temperatures, and  $v = 2048$  at the higher temperatures.

The increase, with dilution, in the "constants" of bromsuccinic acid may be accounted for by the fact that the second hydrogen ion probably begins to split off at higher dilutions, and the acid behaves as if it were dibasic. White and Jones observed a similar action in case of malonic, maleic, fumaric, succinic acids, etc.

Walden <sup>(1)</sup> has carried out a careful and elaborate set of experiments with substituted malonic acids, working at only one temperature,  $25^{\circ}$ . Our results are in accord with his. Arranging these acids in the order of their strengths we have:

Acid	$K \times 10^4, 25^{\circ}$	$K \times 10^4, 65^{\circ}$
Dimethyl malonic	7.45	7.01
Butyl malonic	10.8	9.4
Ethyl malonic	12.3	10.0
Isopropyl malonic	13.2	11.3
Benzyl malonic	15.5	12.0
Allylmalonic	16.0	13.4
Malonic*	16.3	-----
Methyl ethyl malonic	16.5	14.6
Diethyl malonic	74	50
Dipropyl malonic	113	79

(1) Z physik Chem. 8, 433 (1891)

\*Value found by Walden.

REVISED

Walden's arrangement is precisely the same, excepting that he places malonic acid below methyl-ethyl-malonic. Our observations then agree with his--malonic acid is stronger than any of its monosubstitution products, and is weaker than any of the disubstituted acids, with the exception of dimethyl malonic acid. Temperature seems to have no influence on the relative strengths of the acids. There seems to be no rule governing the order in which the monosubstituted malonic acids fall. The strength of the disubstituted acids increases with increasing molecular weight, as Walden has pointed out. Combining his values and ours for disubstituted malonic acids:

Acid	Molecular Weight	$K \times 10^4, 25^\circ$
Dimethyl malonic	132	7.45
Ethyl-methyl-malonic	146	16.5
Diethyl malonic	160	74
Diallyl malonic*	184	76
Dipropyl malonic	188	113
Benzyl-ethyl-malonic*	222	146
Dibenzyl malonic*	284	410

The asterisked acids were worked by Walden.

In this connection Ostwald <sup>(1)</sup> has taken the conductivity of benzal malonic acid from the formula  $C_6H_5 CH = C(COOH)_2$ . We should scarcely know whether to call it a mono or disubstituted

---

(1) Z physik. Chem., 3, 369 (1889)





acid. Both hydrogens of malonic acid are replaced, but by a single bivalent group. The behavior of this acid is equally perplexing. Its constant is 40.8--higher than any monosubstituted acid, but too low for the disubstitution table, where its place should be between dipropyl and benzyl- ethyl malonic acids, according to its molecular weight, 192.

The percentage temperature coefficients of these substituted malonic acids, never decreased with increasing dilution. This decrease was observed by White and Jones <sup>(1)</sup> to be a general occurrence. Wightman and Jones <sup>(2)</sup> also included this relation in the summary of their work, though most of their data seems to point in the opposite direction. In this we agree with the latter investigators.

Isomeric acids have long been the subject of experimental and theoretical investigation. Why do they behave differently? Are there no definite rules governing their action? Ostwald <sup>(3)</sup>, Walker <sup>(4)</sup> and very recently Derick <sup>(5)</sup> have worked on the correlation of ionization and structure for such acids, and on the nature of different substituting groups.

The following relation seems to hold for a limited number of cases, which have presented themselves in this investigation:

- 
- (1) Am. Chem. J., 44, 198 (1910)
  - (2) Ibid 46, 111 (1911)
  - (3) Z physik Chem., 3, 170 (1889)
  - (4) J. Chem. Soc., 61, 605 (1892); 67, 147 (1895)
  - (5) J. Am. Chem. Soc., 33, 1881 (1911); 34, 74 (1912)



In the case of isomeric acids containing two carboxyl groups, the acid with these groups in the "ortho" or the "cis" position is always the stronger. For example:

O. Phthalic  $K = 12.1$

m Phthalic  $K = 2.87$

and again,

Maleic  $K = 154$

Fumaric  $K = 11.1$

The more hydrated an acid is in solution the less its conductivity, other things being equal. If, of two isomeric acids, the one readily forms an anhydride on coming out of solution, while the other retains the constituents of water, it seems fair to assume that the former, in solution, will be the less hydrated--and therefore show the greater molecular conductivity. When it comes to measuring the limiting conductivities ( $M_{\infty}$ ) for these acids, the case is entirely different. The sodium salt of (o) phthalic, or maleic, or any other acid can not form an anhydride. Therefore, in solution there is no reason why it should be less hydrated than its isomer. And since it actually shows the same molecular conductivity, it is probably hydrated to exactly the same extent. So--as has long been known--isomeric acids should have, and actually do have, the same  $M_{\infty}$ . The hydrated acid with a small molecular conductivity will give a smaller percentage dissociation when divided by  $M_{\infty}$  than the unhydrated acid with the larger molecular conductivity, when divided by the same  $M_{\infty}$ . Therefore its constant will be smaller, or, as we say, the acid will be weaker.



In the case of amino acids the proximity of the substituting groups might be expected to facilitate the formation of inner salts. In this connection we have compared results obtained for metanilic and sulphanilic acids. Also for ortho and para amino benzoic acids. In each case the acid with neighboring groups gives more evidence of inner salt formation than does its isomer. Under the discussion of the amino acids, we enumerated some of the characteristics due to this inner salt formation. The percentage temperature coefficients were exceptionally large; the temperature coefficients expressed in conductivity units increased with rise in temperature; the percentage dissociation increased with rise in temperature. By comparing the following data it will be seen that metanilic exhibits these characteristics in a more striking degree than does sulphanilic acid.

#### PERCENTAGE TEMPERATURE COEFFICIENTS

$v = 32$	$35^{\circ}-50^{\circ}$	$50^{\circ}-65^{\circ}$
Metanilic acid	2.66	2.23
Sulphanilic acid	2.28	1.89

#### TEMPERATURE COEFFICIENTS (Cond units)

$v = 1024$	$35^{\circ}-50^{\circ}$	$50^{\circ}-65^{\circ}$
Metanilic acid	3.45	3.82
Sulphanilic acid	4.36	4.37



## DISSOCIATION CONSTANTS

	0°	65°	%increase
Metanilic acid	0.90	5.33	600
Sulphanilic acid	3.28	13.4	400

Moreover metanilic acid conducts less than sulphanilic acid; and inner salts have lower conductivity than the acids from which they are formed. This seems sufficient evidence that meta amino acids have greater salt forming power than the para amino acids.

By a similar comparison of the data of White and Jones<sup>(1)</sup> on ortho and para amino benzoic acids, it will be seen that the para acid again forms less of the inner salt than does its isomer.

In the introduction to this article we stated that we would compare a few conductivity measurements made, with the same acid, by different investigators. Because of disagreements in the results obtained by our predecessors, we repeated the measurements for the following acids at higher temperatures.

---

(1) Am. Chem. J., 44, 195-6 (1910)





Salicylic Acid 35°  
Molecular Conductivity

(1)		(2)	
v. White and Jones		Clover and Jones	Springer
64	92.80	94.27	93.64
128	125.1	126.1	126.0
512	207.0	210.3	209.7
1024	255.4	253.3	255.0
2048	295.7	294.5	294.6

In this case our results appear to be about the mean between the results of White and Jones, and Clover and Jones. The agreement in the following acid is more satisfactory

(o) Phthalic Acid 35°  
Molecular Conductivity

v	White and Jones	Clover and Jones	Springer
64	98.48	96.20	96.31
128	128.9	128.2	128.06
512	212.5	213.3	212.8
1024	259.7	258.6	258.5
2048	306.0	301.9	302.7

We have also had the opportunity of repeating measurements made by earlier investigators, and comparing our results:

---

(1) Am. Chem. J., 44, 189 (1910)

(2) Ibid 43, 213 (1910)



Ethyl-malonic Acid 25°  
Molecular Conductivity

v	Ostwald <sup>(1)</sup>	Walden <sup>(2)</sup>	Springer
32	64.5	65.07	64.42
128	115	117.6	114.55
512	188	192	188.9
1024	229	236	231.2

These are what we might call our average agreements.

There are, of course, cases in which the difficulties are greater--an acid such as acetylsalicylic, which hydrolyzes and decomposes.

Acetyl-salicylic Acid 25°  
Molecular Conductivity

v	Ostwald <sup>(3)</sup>	Springer
128	65.7	60.6
512	117.2	109.3
1024	151.5	139.3

Such a case as this, however, is really exceptional.

(1) Z. physik. Chem., 3, 284 (1889)

(2) Ibid 8, 449 (1891)

(3) Ibid 3, 264 (1889)

# THE UNIVERSITY OF CHICAGO

OFFICE OF THE DEAN OF STUDENTS

1950-1951	1951-1952	1952-1953	1953-1954
1954-1955	1955-1956	1956-1957	1957-1958
1958-1959	1959-1960	1960-1961	1961-1962
1962-1963	1963-1964	1964-1965	1965-1966
1966-1967	1967-1968	1968-1969	1969-1970

THE UNIVERSITY OF CHICAGO  
OFFICE OF THE DEAN OF STUDENTS  
540 EAST 58TH STREET, CHICAGO, ILLINOIS 60637  
TELEPHONE 373-4141

## ADMISSIONS

1950-1951

1951-1952	1952-1953	1953-1954
1954-1955	1955-1956	1956-1957
1957-1958	1958-1959	1959-1960
1960-1961	1961-1962	1962-1963
1963-1964	1964-1965	1965-1966
1966-1967	1967-1968	1968-1969
1969-1970	1970-1971	1971-1972

## GRADUATE STUDIES

1950-1951	1951-1952	1952-1953	1953-1954
1954-1955	1955-1956	1956-1957	1957-1958
1958-1959	1959-1960	1960-1961	1961-1962
1962-1963	1963-1964	1964-1965	1965-1966
1966-1967	1967-1968	1968-1969	1969-1970
1970-1971	1971-1972	1972-1973	1973-1974

## SUMMARY

-:-

Most of the facts established by White and Jones<sup>(1)</sup> and Wightman and Jones<sup>(2)</sup> have been confirmed by the present work. Some of the more obvious of these relations have not been discussed in detail, since reference to our data will suffice to show that they hold.

1. The percentage temperature coefficients of conductivity of the organic acids are generally small, and of the same order of magnitude, and decrease with rise in temperature.

2. The temperature coefficients, expressed in conductivity units, increase rapidly with dilution and decrease with rise in temperature. The stronger the organic acid, the larger these conductivity units.

3. The percentage temperature coefficients of the amino acids are exceptionally large, and the coefficients expressed in conductivity units increase with rise in temperature. The internal salt-forming power of these amphoteric electrolytes explains this behavior.

4. The conductivity of most organic acids is a parabolic function of the temperature, as has been pointed out by Euler<sup>(3)</sup> This may be seen by comparing observed values with those calculated from the formula,

$$\lambda = a + bt - ct^2$$

---

(1) Am. Chem. J., 44, 198 (1910)

(2) Ibid 46, 111 (1911)

(3) Z. physik. Chem., 21, 257 (1896)



5. Change in temperature does not seem to influence the relative strengths of organic acids.
6. Strong organic acids do not obey the Ostwald dilution law.
7. Most dibasic organic acids dissociate like monobasic acids.
8. The migration velocities of the anions of organic acids are a function of the number of atoms present in the anions, and  $M_{\infty}$  values for dibasic acids may be found by means of this principle.
9. The relation of dissociation of organic acids to temperature seems to be irregular. In general the maximum dissociation has been reached at temperatures worked with. The dissociation of only the amino acids increases at temperatures higher than  $50^{\circ}$ .
10. Isomeric acids do not behave similarly as regards change in their dissociation.
11. A relation has been found, which possibly connects the behavior of some isomeric acids with their structure and power to form inner salts and anhydrides.





## BIOGRAPHICAL

---

Alfred Springer, Jr., was born in Cincinnati, on November 1st, 1888. His public and high school education was obtained at Norwood, Ohio.

He entered Yale University in 1905, receiving the degree of Bachelor of Arts in 1909. Since then he has been a student in chemistry at Johns Hopkins University, where he was appointed Fellow for the year 1911-1912.

---



















